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Signed

Dated 18 FEB 1999

Patents Act 1977

Patent Office

17FEB98 E338695-1 002831
P01/7700 25.00 - 9803249.3

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

17 FEB 1998

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

57.291 UK

2. Patent application number
(The Patent Office will fill in this part)

9803249.3

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Sofitech N.V.

Rue de Stalle 140
B-1180 Brussels

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

Belgium

4. Title of the invention

Anti-accretion additives for drilling fluids

5. Name of your agent *(if you have one)*

MIRZA, Akram Karim

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

c/o Schlumberger Cambridge Research Ltd
High Cross, Madingley Road
Cambridge
CB3 0EL

Patents ADP number *(if you know it)*

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

YES

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	-
Description	7
Claim(s)	2
Abstract	1
Drawing(s)	-

10. If you are also filing any of the following, state how many against each item.

Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	1 (plus 2 copies)
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	-

11. I/We request the grant of a patent on the basis of this application

Signature [signature] Date 16 February 1998

12. Name and daytime telephone number of person to contact in the United Kingdom MIRZA, Akram Karim 01223-325268

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

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Anti-accretion additives for drilling fluids

This invention relates to anti-accretion additives for drilling muds.

BACKGROUND OF THE INVENTION

Bit-balling and cuttings accretion are problems encountered when drilling shales, particularly with water-based muds. Shale cuttings can adhere to each other and to the bottom hole assembly and cutting surfaces of the bit. Gradually a large plastic mass builds up which can block mud circulation and reduce rates of penetration. There is a "danger zone" of clay plasticity for balling and accretion, related to the water content of the clay or shale, which can be defined in terms of the Atterberg limits of soil mechanics. In the dry zone the clay has too little water to stick together and it is a friable and brittle solid. In the wet zone the material is essentially liquid like with very little inherent strength and can be washed away. Intermediate to these zones, i.e., in the danger zone, the shale is a sticky plastic solid with greatly increased agglomeration properties and inherent strength.

When cuttings are exposed to conventional water-based muds they usually imbibe water and pass rapidly through these different zones, eventually dispersing. However recent advances in drilling fluid technology have developed highly inhibitive muds which appear to reduce the hydration of shale and in doing so maintain the cuttings in the danger or plastic zone contributing to increased accretion and bit-balling. Field experiences with glycol, phosphate and silicate muds in particular have shown accretion problems.

US patent 5,639,715 describes additives for bit-balling prevention based on sulphonosuccinate chemistry.

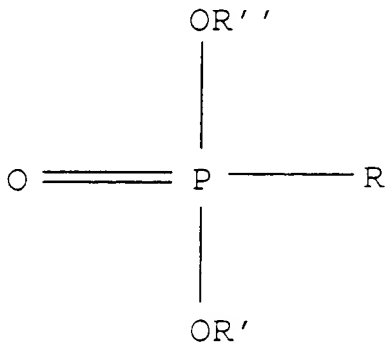
Phosphorus based additives and compound have been used in the oilfield industry mainly for the purpose of enhancing oil recovery from production wells.

It is the object of the present invention to find alternatives to the known methods of preventing accretion.

SUMMARY OF THE INVENTION

The invention is an additive for drilling mud. The additive reduces the accretion and bit-balling tendencies of cuttings exposed to said muds. The additives are based on phosphonate chemistry, and are preferably of the general class:

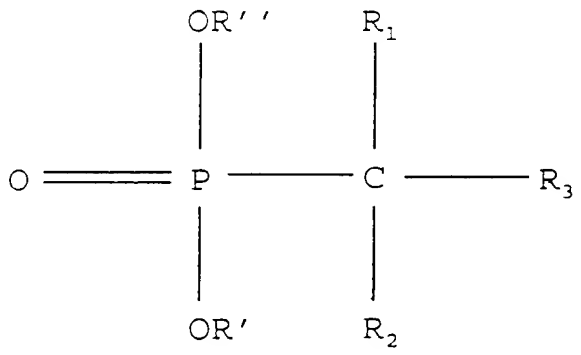
(I)



where R, R' and R'' are groups of non-polymeric character, i.e., comprising 0 - 100 carbon atoms.

In a more preferred embodiment, the additives are based on the formula

(II)



where R_1, R_2 and R_3 are groups of non-polymeric character.

In another preferred embodiment of the invention, the additive is a phosphor derivative of the succinic acid or short chain phosphorylated hydrocarbons.

Additives according to the invention are added to the drilling fluid at levels 0.1-10%, preferably 1-5%, weight by volume (%kg/liter).The drilling fluid itself may be oil based, though it is recognized that accretion tends to be less pronounced in drilling muds of this kind. Therefore, the preferred drilling fluid in accordance with the present invention is water based, even more preferably a reactive anionic based drilling fluid, such as silicate or phosphate based muds. Further additives as known in the art may be added to impart other desired properties to the mud system.

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description below.

MODE(S) FOR CARRYING OUT THE INVENTION

A test used to determine the anti-accretion properties of additives involves squeezing shale or clay cuttings between two steel plates with a given force causing them to stick to each other and the plates. The force required to slide the plates apart is then determined using a force gauge or spring balance.

Oxford clay cuttings of size 2-4mm were soaked in the test fluid for 15 minutes. The excess mud was drained from the cuttings using a sieve (500 micron mesh). A small pile of cuttings (5-10g) was put onto the base plate of the tester. The pile was roughly levelled and the top plate replaced over the cuttings. A PTFE spacer was placed on top of the top plate. A screw-mounted plunger in the tester housing was wound down until it made contact with the spacer. A torque wrench was used to tighten the plunger onto the top plate. The standard torque was 75 inch-pounds (~9N.m). Immediately on reaching this value, the plunger was wound back sufficiently to remove the spacer. A force gauge or spring balance was then connected to the top plate. The tension on the top plate was then increased by pulling on the force gauge until the plate breaks free from the cuttings bed. The maximum force recorded was the freeing force for the plate or accretion value. Values can range from 1.0 to above 20.0 kg force.

The phosphonate based additives tested in accordance with the above procedure are added to a water-based mud containing tetrapotassium pyrophosphate (TKPP) and consisting of

1000 ml fresh water
85.5 g tetrapotassium pyrophosphate

2.85 g xanthan gum

11.4 g carboxy methyl cellulose (low viscosity grade)

42.75 g simulated drill solids

barite to density 1.08 sg.

NaOH to pH 9.2

biocide

Baseline accretion values were established as:

Simple polymer mud	5 kg
TKPP mud	21.7 kg

The anti-accretion additives were then added to the TKPP mud at levels of 1-5%.

Additives which reduced the accretion value from >10 kg to 9 kg or below were:

- Hydrolysed polymaleic acid
- 3-phosphonopropionic acid
- succinic acid
- propyl phosphonic acid
- dibutyl-butyl phosphonate
- hydroxyphosphonoacetic acid
- dimethylpropyl phosphonate
- phosphorous acid
- diethyl-ethylphosphonate
- ethylmethacylate phosphate
- tri-ethyl phosphonoacetate
- tetramethyl phosphonosuccinate
- phosphonosuccinic acid
- 2-hydroxyethyl phosphonic acid.

The last five additives (Additives 9-14) were the found most effective. For those the following values were recorded:

TKPP mud + (%)additive:	Accretion value
1% diethyl-ethylphosphonate	8 kg
5% diethyl-ethylphosphonate	7 kg
5% ethylmethacrylate phosphate	6 kg
1% tri-ethyl phosphonoacetate	8 kg
5% tri-ethyl phosphonoacetate	5 kg
5% tetramethyl phosphonosuccinate	7 kg
5% phosphonosuccinic acid	7 kg
5% 2-hydroxyethyl phosphonic acid.	7 kg

In a second series of tests with the additives, silicate mud of the following composition was used:

1000 ml sea water
131 g Na silicate, a solution of 14% NaOH and 27% SiO_2
117.5 g KCl
20 g Polyanionic cellulose
5 g Xanthan gum
NaOH to adjust pH to 12.

Baseline accretion values were established as:

simple polymer mud	9.5 kg
silicate mud	17.7 kg

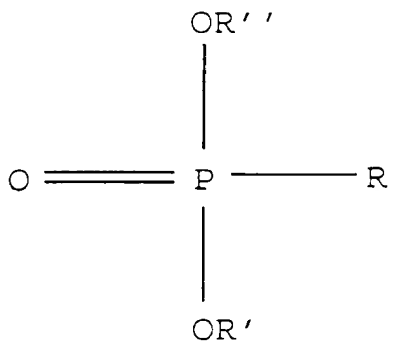
The anti-accretion additives were tested in the silicate mud at 1% (w/v):

Silicate mud + (1%) additive:	Accretion value
diethyl-ethylphosphonate	11.1 kg
tri-ethyl phosphonoacetate	11.35 kg
tetramethyl phosphonosuccinate	9.96 kg
phosphonosuccinic acid	10.8 kg
2-hydroxyethyl phosphonic acid	11.4 kg

In most cases the accretion value has been reduced significantly, down to the levels of a simple polymer mud.

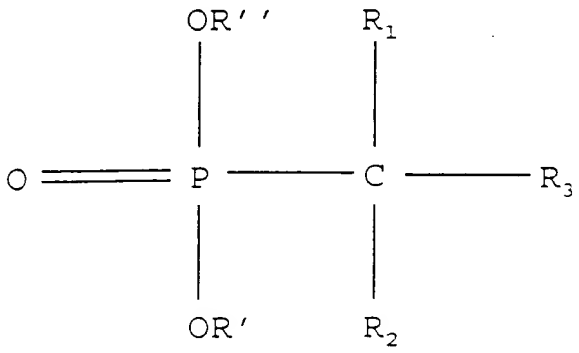
CLAIMS

1. Additive for a drilling fluid, consisting of a compound in accordance with the formula



where R, R' and R'' are groups of non-polymeric character.

2. The additive of claim 1, consisting of a compound in accordance with the formula



where R_1, R_2 and R_3 are groups of non-polymeric character.

3. The additive of claim 1, based on a phosphor derivative of the succinic acid.

4. The additive of claim 1, based on a short chain phosphorylated hydrocarbon.

5. Drilling fluid comprising an additive in accordance with claim 1.

6. The drilling fluid of claim 5, comprising an additive in accordance with claim 1 in a concentration of up to about 10% weight by volume.

7. The drilling fluid of claim 5, being a water-based drilling fluid.

8. The drilling fluid of claim 5, being a reactive anionic drilling fluid.

9. The drilling fluid of claim 5, being a phosphate-based drilling fluid.

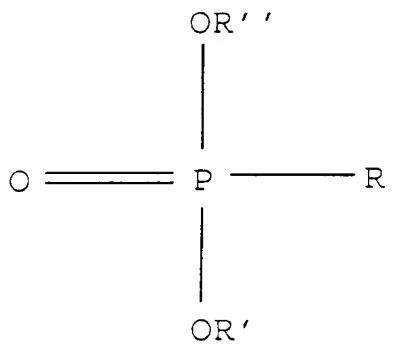
10. The drilling fluid of claim 5, being a silicate-based drilling fluid.

11. Method of preventing accretion of cuttings in a borehole, said method comprising the step of adding to a drilling fluid an additive in accordance with claim 1 prior to or during a drilling operation.

12. The method of claim 11, wherein the additive is added in a concentration of up to about 10% weight by volume of the drilling fluid.

ABSTRACT

Additives for drilling fluids, in particular for water-based drilling fluids are described which when added to the fluid at levels of up to 10% weight by volume reduces the accretion and bit-balling tendencies of shale cuttings exposed to said fluids. The additives are based on phosphonate chemistry, and are of the general class:



where R, R′ and R′′ are groups of non-polymeric character.